

**PROCESS MODELING AND COMPARISON STUDY OF ACID GAS
REMOVAL UNIT BY USING DIFFERENT AQUEOUS AMINES**

FLORENCE WEDNNA SANGGIE

**A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)**

**Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang**

April 2011

ABSTRACT

Natural gas need to be purified to meet the quality standards since it contains impurities such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S), which are they are the main acid gases that as its can cause corrosion, reduce the heating and sales value of gas. Aqueous amine solutions are proven to be practical solvents for the treatment of natural gas. By simply changing their amine solutions, many inefficient acid gas removal units can be optimized. Acid gas removal unit (AGRU) simulation is an essential tool for control and operations in gas processing plant because it can be used to stimulate and analyses the under different operating conditions. In this study, Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) will be use to model the acid gas removal unit process by using Aspen Hysys. MEA is effective at removing almost all hydrogen sulfide and carbon dioxide among the other amines. Meanwhile, DEA and MDEA allows for some carbon dioxide to be left in the sweet gas that are suit for gas steams with less stringent product specifications. Accordingly, the heat consumption at the regenerator was in the following order $\text{MEA} > \text{DEA} > \text{MDEA}$. Improvement studies were extended to the effect of increasing the circulation rate, amines concentration and reboiler heat consumption. By increasing the circulation rate, MEA causes the CO_2 to be almost completely absorbed in the column even at the lowest low circulation rate followed by DEA and. MDEA. By increasing concentration of amine, MEA and MDEA showed at 15 wt % or greater is required to achieve the specified acid gas removal and 25 wt % for DEA. One also can reduce heat of reaction by changing from a primary to secondary amine which both gives almost the same acid gas removal efficiency. This research can broaden by using different simulation tools available model the AGRU and also perform the comparison on the cost estimating for MEA, DEA and MDEA.

ABSTRAK

Gas Asli perlu diproses atau ditapis untuk memenuhi standard kerana ia mengandungi benda asing seperti karbon dioksida (CO_2) dan hidrogen sulfida (H_2S), yang merupakan gas-gas asid utama yang boleh menyebabkan hakisan, mengurangkan nilai pemanasan dan nilai jualan gas. Amina terbukti sebagai penyelesaian pratikal untuk menapis gas asli. Dengan menukar penyelesaian jenis penggunaan amina, banyak acid removal unit (AGRU) dapat dioptimumkan. AGRU simulasi adalah alat yang penting untuk kawalan dan operasi di pusat pemprosesan gas kerana ia boleh digunakan untuk menganalisis pada operasi yang berbeza. Dalam kajian ini, Monoethanolamine (MEA), Dietanolamine (DEA) dan Methyldiethanolamine (MDEA) akan digunakan untuk model AGRU dengan menggunakan Aspen Hysys. MEA berkesan menyingkirkan hampir semua hidrogen sulfida, dan karbon dioksida berbanding dengan amina lain. Sementara itu, DEA dan MDEA membenarkan beberapa karbon dioksida dibiarkan dalam gas manis yang sesuai untuk stim gas dengan spesifikasi produk yang rendah. Dengan demikian, penggunaan tenaga di Regenerator adalah mengikut urutan MEA berikutan DEA > MDEA. Kajian diteruskan dengan kesan meningkatkan tahap sirkulasi, kepekatan amina dan pengambilan reboiler panas. MEA adalah yang terbaik kerana CO_2 yang akan hampir sepenuhnya terserap bahkan pada peredaran rendah terendah. Dengan meningkatkan kepekatan amina, MEA dan MDEA menunjukkan sebanyak 15% wt atau lebih besar diperlukan bagi mencapai jumlah penyingkiran gas asid dan 25% wt untuk DEA. Dengan meningkatkan. Untuk mengurangkan penggunaan tenaga, menukar dari amina primer ke sekunder yang baik memberikan hampir gas asid kecekapan penyerapan yang sama. Penyelidikan ini dapat diperluaskan lagi dengan menggunakan alat simulasi pelbagai model dan juga melakukan perbandingan terhadap kos untuk MEA, DEA dan MDEA.

TABLE OF CONTENT

| CHAPTER | TITLES | PAGE |
|----------|--|------|
| | DECLARATION | v |
| | DEDICATION | vi |
| | ACKNOWLEDGEMENTS | vii |
| | ABSTRACT | viii |
| | ABSTRAK | ix |
| | TABLE OF CONTENTS | x |
| | LIST OF TABLES | vii |
| | LIST OF FIGURE | viii |
| | LIST OF ABBREVIATIONS | xiv |
| | LIST OF SYMBOLS | xv |
| 1 | INTRODUCTION | |
| | 1.1 Natural Gas and Impurities Removal | 1-3 |
| | 1.2 Problem Statement | 4 |
| | 1.3 Objectives | 5 |
| | 1.4 Scope of Study | 5 |
| | 1.5 Rationale & Significance of Study | 5 |
| 2 | LITERATURE REVIEW | |
| | 2.1 Introduction | 6 |
| | 2.2 Amines | |
| | 2.2.1 Monoethanolamine (MEA) | 7-8 |
| | 2.2.2 Diethanolamine (DEA) | 8 |
| | 2.2.3 Methyldiethanolamine(MDEA) | 9-11 |

| | | |
|----------|---|-------|
| | 2.3 Comparative study of MEA, DEA and MDEA as chemical solvent | 11-13 |
| | 2.4 Acid Gas | 14-15 |
| | 2.5 Acid Gas Removal Processes | 16-17 |
| | 2.6 Process Chemistry | 18-20 |
| | 2.7 Hysys Process Simulation Package | 21 |
| 3 | METHDOLOGY | |
| | 3.1 Introduction | 22-23 |
| | 3.2 Obtain the flow sheet and design data of AGRU | 24 |
| | 3.3 Select the suitable package for AGRU simulation process | 25 |
| | 3.4 Simulate AGRU process using MEA, DEA and MDEA as a chemical solvent | 26-30 |
| | 3.5 Compare the process performance | 31 |
| | 3.6 Suggestion for improvement | 31 |
| 4 | RESULT & DISCUSSION | |
| | 4.1 Introduction | 32-34 |
| | 4.2 Absorption efficiency of amines | 34-37 |
| | 4.3 The effect of Circulation rate | 37-38 |
| | 4.4 The effecr of Amine Concentration | 38-41 |
| | 4.5 Improvement on heating requirement | 41-43 |
| 5 | CONCLUSION | 44 |
| | RECOMMENDATION | 45 |
| | REFERENCES | 46-48 |
| | APPENDICES | 49 |

LIST OF TABLE

| FIGURE NO. | TITLE | PAGE |
|-------------------|---|-------------|
| 2.1 | The physical properties of MEA, DEA and MDEA | 10 |
| 2.2 | Typical operating conditions and data for amines | 11 |
| 2.3 | Typical composition of natural gas mixture | 15 |
| 4.1 | Simulation Results of Amine Acid Gas Absorber | 33 |
| 4.2 | Simulation Result of mole component of H ₂ S and CO ₂ in sweet gas with different amine concentration | 39 |
| 4.3 | Simulation Result of Reboiler Duty at Regenerator with different concentration of MEA | 41 |
| 4.4 | Simulation Result of Reboiler Duty at Regenerator with different concentration of DEA | 42 |

LIST OF FIGURES

| FIGURE NO. | TITLE | PAGE |
|------------|--|------|
| 2.1 | Schematic of simple acid gas removal unit | 16 |
| 3.1 | Flowchart of methodology | 23 |
| 3.2 | Process Flow Diagram of AGRU | 24 |
| 3.3 | Fluid Package Basis (Amine fluid Package) | 25 |
| 3.4 | Component selection windows | 26 |
| 3.5 | Simulation approach for the absorber and regenerator | 27 |
| 3.6 | Simulation Environment | 28 |
| 3.7 | Converged window of the Absorber | 29 |
| 3.8 | Converged window for regenerator unit | 30 |
| 4.1 | The absorption performance by the number of stage (height of column) | 35 |
| 4.2 | CO ₂ Absorption efficiency with increasing CO ₂ loading | 35 |
| 4.3 | CO ₂ Absorption efficiency with increasing liquid load | 36 |
| 4.4 | Effect of Circulation Rate on CO ₂ composition in Sweet Gas | 37 |
| 4.5 | Effect of increasing the concentration of amines to the CO ₂ in the Sweet Gas | 39 |
| 4.6 | Effect of increasing amine concentration to the CH ₄ losses in Sweet Gas | 40 |
| 4.7 | Effect of increasing MEA concentration to the reboiler duty | 42 |
| 4.8 | Effect of increasing DEA concentration to the Reboiler duty | 43 |

LIST OF ABBREVIATION

| | | |
|--------------------------------|---|------------------------------|
| CH ₄ | - | Methane |
| C ₂ H ₆ | - | Ethane |
| C ₃ H ₈ | - | Propane |
| C ₄ H ₁₀ | - | Butane |
| C ₅ H ₁₂ | - | Pentane |
| CO ₂ | - | Carbon Dioxide |
| COS | - | Carbonyl Sulfide |
| CS ₂ | - | Carbon disulfide |
| MDEA | - | Methyldiethanolamine |
| MEA | - | Monoethanolamine |
| DEA | - | Diethanolamine |
| H ₂ S | - | Hydrogen sulfide |
| AGRU | - | Acid Gas Removal Unit |
| Ppm | - | Part Per Million |
| TEA | - | Triethanolamine (TEA) |
| TSCF | - | Trillion standard cubic feet |

LIST OF SYMBOLS

°C : Celsius

% : Percent

CHAPTER 1

INTRODUCTION

1.1 NATURAL GAS AND IMPURITIES REMOVAL

Natural gas has now become a crucial component of world's supply energy. The demand for natural gas has risen drastically over the past few years due to its importance in various industries and also for the domestic purposes. Malaysia is ranked 14th in the world in terms of its gas reserves and as of 1st January 2008, the natural gas reserves in Malaysia stood at 88.0 trillion standard cubic feet (tscf) or 14.67 billion barrels of oil equivalent, approximately three times the size of crude oil reserves of 5.46 billion barrel (Gas Malaysia, 2008).

The production of Natural Gas started millions of years ago. It is combustible mixture hydrocarbon gases with colorless, shapeless, and odorless characteristics. It is a subcategory of petroleum that is a naturally occurring, complex mixture of hydrocarbons, with a minor amount of inorganic compounds. It is formed from the remains of ancient microorganisms as well as plant and animal matter that have undergone conditions of extreme heat and pressure over very long periods of time. Intense compression and high temperature conditions cause carbon bonds in the organic matter to break down, a chemical transformation resulting in the formation of natural gas and other fossil fuels.

Natural gas has to be purified to meet the quality standards specified by the major pipeline transmission and distribution companies since the natural gas contains others impurities such as liquids (water, heavier hydrocarbons), sand, mercury and other gasses like nitrogen, helium and acid gases (carbon dioxide, hydrogen sulfide

and mercaptans such as methanethiol and ethanethiol). Carbon dioxide (CO_2), hydrogen sulfide (H_2S) and other sulfide compound are the main acid gases that may require complete or partial removal as they can cause corrosion, reduce the heating and sales value of the gas to meet gas purchaser's acceptance in distribution specification, safety and transport requirement. Those quality standards vary from pipeline to pipeline and are usually a function of a pipeline system's design and the markets that it serves. Generally, one of the standards specifies that natural gas contain no more than trace amounts of components such as acid gases. In general, an acid gas pipeline specification is 4.0 ppm H_2S and 1.0% CO_2 (Arnold et.al, 2007). At 0.13 ppm by volume, H_2S can be sensed by smell. At 4.6 ppm the smell is quite noticeable (Fahim et.al, 2003).

However, one of the challenges of operating the gas processing plant is how the operational procedures can be adjusted to meet the dynamic and future demands of customers. Thus, acid gas removal simulation is an essential tool for control and operations in gas processing plant because it can be used to stimulate and analyses the acid gas removal unit (AGRU) under different operating conditions. Analyses of chemical and phase equilibrium are needed whenever significant changes in patterns and magnitudes of demand or supplies occur (Alfadala, 2009). In the absence of such analyses, the operational procedures may not be optimal, resulting in unnecessarily high operating cost.

The main removal processes are based on absorption and selectivity of the solvent with respect to acid gases is based on an affinity of the chemical or physical type. Removal of H_2S and CO_2 from natural gases by using alkanolamines technology has been around for decades. By simply changing their amine solutions, many inefficient acid gas removal units can be optimized. Suitable amine selection can drastically reduce the regeneration energy requirement and solution circulation rate. Hence, the process conditions can have a dramatic impact on the overall costs associated with AGRU.

Industrially important alkanolamines for this AGRU are monoethanol amine (MEA), diethanol amine (DEA) and methyldiethanol amine (MDEA). Monoethanolamine (MEA), a primary amine, has been used extensively because of

its high reactivity and low solvent cost. MEA is used in solution in concentration of 10% to 15% by weight. MEA on the other hand, reacts irreversibly with COS, CS₂ and mercaptans. It is very reactive, it absorbs H₂S and CO₂ at once and not selectively. Its relatively high vapor pressure causes larger losses compared with the other amines and for this reason, it is mainly used for intensive purification. Diethanolamine (DEA) helps to overcome the limitation of MEA, and can be used in the presence of COS and CS₂. Methyldiethanolamine (MDEA) are commonly used as chemical solvent for the removal of CO₂ from gas mixtures or in gas sweetening processes for the extraction of CO₂ and H₂S (Furhacker, Pressl & Allabashi, 2003). It has become the industry's standard for selective treating application which do not require removal significant quantities of COS, mercaptans and other trace of sulphur-containing contaminant (Okimoto, 1993). Process modelling, simulation and optimisation are practiced to reduce production cost, shorten research and development period, increasing the process effectiveness, improving product quality, handle the sophisticated problem in industry (Turton *et. al*, 1998). Process simulator, such as Aspen Hysys simulator, plays an important role to accomplish these objectives. Simulator can also be used to design and scale up a new plant, or optimise an existing plant.

1.2 PROBLEM STATEMENT

Since the 1960s and 1970s, several amines have come into general use, but there is little information available on which amine is best suited to a particular service. Many inefficient amine gas sweetening units can be optimized by simply changing the amines.

Between 50–70% of the initial investment for an amine-sweetening unit is directly associated with the magnitude of the solvent circulation rate and another 10–20% of the initial investment depend on the regeneration energy requirement. Between 50–70% of the initial investment for an amine-sweetening unit is directly associated with the magnitude of the solvent circulation rate and another 10–20% of

the initial investment depend on the regeneration energy requirement. Approximately 70% of gas sweetening plants operating costs, excluding labour expenses, is due to the energy required for solvent regeneration (Khakdaman et. al, 2008). Each amine has a unique set of properties which make it desirable under certain conditions and undesirable under other conditions. The choice of the type of amine will affect the required circulation rate of amine solution, the energy consumption for the regeneration and the ability to selectively remove either H_2S alone or CO_2 alone if desired. The selection of amines best suited to the process conditions can have a dramatic impact on the overall costs associated with a sweetening unit.

Therefore, it is important to know the performance of MEA, DEA and MDEA as a chemical solvent in acid gas removal unit and the using of Aspen Hysys for simulated this process. The removal of acid gas impurities such as CO_2 and H_2S from natural, refinery and synthesis gas streams is a significant operation in gas processing. The specifications on acid gas contents are essential by safety requirement (very high toxicity of H_2S), transport requirements (need to avoid corrosion in pipeline and crystallization in case of liquefaction) and distribution specification (commercial gas).

1.3 OBJECTIVES

The main objective of this study is to model the acid gas removal unit (AGRU) using Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) as the solvent by using Aspen Hysys as computer simulator.

In addition, the other objective of this study is to compare the performance of Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) and develop processes with some improvement in term of the efficiency of the AGRU.

1.4 SCOPE OF STUDY

In this study, software for acid gases removal unit will be needed, that is Aspen Hysys. This software can be used to simulate the acid gas removal plant. One reactive absorption and desorption columns will be used to perform this simulation program.

Next, studies on Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) as the chemical solvent in the absorption column for the simulated acid gas removal process.

1.5 RATIONALE AND SIGNIFICANCE OF STUDY

The study is essential, to model and improve the process of acid gas removal based on Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) by using Aspen Hysys.

Additionally, this study also significant, to identified the best chemical solvent for AGRU process by comparing MEA, DEA and MDEA.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Removal of acid gas components such as H_2S , CO_2 and other sulfur species (COS , CS_2 and mercaptans) from natural gas, refinery gas or natural gas liquids by aqueous amines is a regularly encountered operation in the process industry. The removal of acid gases from natural gas is important either to meet certain process specifications or to keep emission limits. The major approach towards acid gas removal is absorption into solution of alkanolamines or potassium carbonate. In the practical application, such absorption plants consist of two gas-liquid reactors operated at different temperatures and pressures: absorber and regenerator. The choice of the type of amine will affect the required circulation rate of amine solution, the energy consumption for the regeneration and the ability to selectively remove either H_2S alone or CO_2 alone if desired. Because of the large scale testing is expensive; it is more practical to use simulation to evaluate each process with different amines.

2.2 AMINES

2.2.1 Monoethanolamine (MEA)

Ethanolamine, also called 2-aminoethanol or monoethanolamine (often abbreviated as MEA), is an organic chemical compound which is both a primary amine (due to an amino group in its molecule) and a primary alcohol (due to a hydroxyl group).

Like other amines, MEA acts as a weak base. Ethanolamine is a toxic flammable corrosive colorless viscous liquid with an odor similar to ammonia. Ethanolamine is commonly called monoethanolamine or MEA to differentiate it from diethanolamine (DEA) and triethanolamine (TEA). Monoethanolamine is produced by reacting ethylene oxide with ammonia. Further treatment with ethylene oxide can yield DEA or TEA or both DEA and TEA. (ICON Group International, 2008).

MEA should commonly be used as a 10 to 20% solution in water. The acid gas loading should usually be limited to 0.3 to 0.4 moles acid gas per mole of amine for carbon steel equipment. MEA itself is not considered to be particularly corrosive. However, its degradation products are very corrosive. CO_2 , CS_2 , SO_2 and SO_3 can partially deactivate MEA, which may essentially require to be recovered with a reclaimer.

Since MEA is primary amine, it has a high pH. This enables MEA solutions to produce gas containing less than 6 mg/ Sm^3 ($\frac{1}{4}$ grains H_2S per 100 Scu.ft) of acid gas at very low H_2S partial pressures. The heat of reaction for CO_2 in MEA is about 1930 kJ/kg of CO_2 (460 kcal/kg of CO_2). The heat of reaction for all amines is a function of loading and other conditions. It varies by only 117 to 138 kJ/kg (28 to 33 kcal/kg) up to about 0.5 mole/mole of total acid gas loadings. Above this loading, the heat of reaction varies considerably and should be calculated as a function of loading. MEA will easily reduce acid gas concentrations to Pipeline Specifications (generally less than 6 mg $\text{H}_2\text{S}/\text{Sm}^3$ gas (0.25 grains per 100 Scu.ft). By proper design

and operation, the acid gas content can be reduced as low as 1.2 mg H₂S/Sm³ gas (0.05 grains per 100 Scu.ft). (Engineering Standard, 1994)

2.2.2 Diethanolamine (DEA)

Diethanolamine, often abbreviated as DEA, is an organic compound which is both a secondary amine and a dialcohol. A dialcohol has two hydroxyl groups in its molecule. Like other amines, diethanolamine acts as a weak base. Other names or synonyms are bis (hydroxyethyl) amine, diethylolamine, hydroxydiethylamine, diolamine and 2,2'-iminodiethanol.

DEA is commonly used in the 25 to 35 mass percent ranges. The loading for DEA is also limited to 0.3 to 0.4 mole/mole of acid gas for carbon steel equipment. When using stainless steel equipment, DEA can safely be loaded to equilibrium. This condition can be considered for carbon steel equipment by adding inhibitors.

The degradation products of DEA are much less corrosive than those of MEA. COS and CS₂ may irreversibly react with DEA to some extent. Since DEA is a secondary alkanolamine, it has a reduced affinity for H₂S and CO₂. As a result, for some low pressure gas streams, DEA cannot produce Pipeline Specification gas. However, certain design arrangement such as split flow may be considered to fulfill the specified requirement. Under some conditions, such as low pressure and liquid residence time on the tray (of about 2 seconds), DEA will be selective toward H₂S and will permit a significant fraction of CO₂ to remain in the product gas. The heat of reaction for DEA and CO₂ is 151 kJ/kg of CO₂ (360 kcal/kg of CO₂) which is about 22% less than for MEA. (Engineering Standard, 1994)

2.2.3 Methyldiethanolamine, MDEA

MDEA which stands for methyldiethanolamine is a psychedelic hallucinogenic drug and empathogen-entactogen of the phenethylamine family. It has a larger capacity to react with acid gases because it can be used in higher concentrations. This advantage is enhanced by the fact that it is reacting with all of the H_2S and only part of CO_2 .

MDEA also delivers energy savings by reducing reboiler duties and lowering overhead condenser duties. MDEA as an absorption solvent of removing acid gases is widely used today in natural gas processing because it possesses the characteristics such as higher H_2S selectivity, bigger absorption capacity, lower regeneration energy, smaller hot degradation and lesser corrosive.

MDEA is most commonly used in the 30 to 50 mass percent ranges. Due to considerably reduced corrosion problems, acid gas loadings as high as 0.7 to 0.8 mole/mole are practical in carbon steel equipment. Since MDEA is a tertiary amine, it has less affinity for H_2S and CO_2 than DEA. Thus, as in the case for DEA, MDEA cannot produce Pipeline Specification gas for some low pressure streams. MDEA has several distinct advantages over primary and secondary amines. These include lower vapor pressure, lower heats of reaction, higher resistance to degradation, fewer corrosion problems and selectivity toward H_2S in the presence of CO_2 .

**The physical properties and the operating condition of MEA, DEA and MDEA are shown in Table 2.1 and Table 2.2*

Table 2.1 The physical properties of MEA, DEA and MDEA
(Kohl and Riesenfeld, 1985)

| PROPERTIES | MEA | DEA | MDEA |
|--|------------|---|-----------------|
| Overall chemical formula | C_2H_7NO | $C_4H_{11}NO_2$ | $C_5H_{13}NO_2$ |
| Molecular weight (kg/kgmol) | 61.08 | 105.14 | 119.17 |
| Melting point ($^{\circ}C$) | 10.5 | 28.0 | -23.0 |
| Boiling point at 101 325 Pa ($^{\circ}C$) | 170.6 | 269.2 | 247.4 |
| Specific gravity (20 $^{\circ}C$ /20 $^{\circ}C$) | 1.0179 | 1.0919 (30 $^{\circ}C$ /20 $^{\circ}C$) | 1.0418 |
| Absolute viscosity at 20 $^{\circ}C$ (Pa.s) | 0.0241 | 0.3800 (30 $^{\circ}C$) | 0.1010 |
| Specific heat at 15.6 $^{\circ}C$ (J/kg.K) | 2546 | 2512 | 2238 |
| Flash point ($^{\circ}C$) | 93.3 | 137.8 | 129.4 |

Table 2.2 Typical operating conditions and data for amines
(Polasek & Bullin, 1994)

| Amine type | MEA | DEA | MDEA |
|--|------------|--------------------------|----------------------|
| Solution strength, wt% | 15-20 | 25-35 | 20-50 |
| Acid gas loading, mole/mole | 0.30-0.35 | 0.30-0.35 | Unlimited |
| Ability for selective absorption of H ₂ S | No | Under Limited Conditions | Under Most Condition |

2.3 COMPARATIVE STUDY OF MEA, DEA AND MDEA AS CHEMICAL SOLVENT

A rate-based model has been developed for the design of acid gas absorbers using aqueous alkanolamine solutions. The model adopts the film theory and assumes that thermodynamic equilibrium among the reacting species exists in the bulk liquid. The program was developed to handle either monoethanolamine (MEA) or diethanolamine (DEA) as chemical solvents. As showed in the result, the number of stages required to meet the H₂S specification is less for MEA as compared with DEA. This is primarily due to the higher reactivity of MEA with the acid gases. The concentration of H₂S drops down to almost zero at about stage 16 for MEA as compared to stage 18 for DEA (Nadhir A. Al-Baghli et.al, 2001).

Additionally, as the pressure is lowered, MDEA becomes less capable of picking up sufficient CO_2 to meet pipeline specification. When large amounts of CO_2 are being passed through to the sweet gas at relatively low pressures, it becomes difficult for MDEA to reach pipeline specification for H_2S if the inlet gas contains more than about 1000 ppm H_2S . At these lower pressures, the addition of a more reactive amine clearly enhances the solution ability to remove CO_2 . Thus, in areas where MDEA cannot meet the residual gas requirements. Usually, to improve the plant performance the mixed amines will be used (Zare Aliabadi et.al, 2009).

From the previous study of John Polasekjerri and A. Bullin on selecting best amines for ARGU, they have compared the few amines such as MEA, DEA, Diglycolamine (DGA) and mixed amines (MEA, DEA and MDEA). The main selection is based on the pressure and acid gas content of the sour gas as well as the purity specification of the sales gas. As the result, MEA is usually not the first amine considered due to its high heat of reaction and lower acid gas carrying capacity per gallon of solution.

However, MEA is still used for plants where the inlet gas pressure is low and pipeline specification gas or total removal of the acid gases is desired. DEA is known as "workhorse" of the industry in late 1960 and early 1970, due to its lower heats of reaction, higher acid gas carrying capacity and resultant lower energy requirements. DEA have potential for selective H_2S removal from streams containing CO_2 under certain conditions.

Depending on the application, MDEA has some outstanding capabilities. Due to its low heat of reaction, it can be used in pressure swing plants for bulk acid gas removal. MDEA is currently best known for its ability to preferentially absorb H_2S and is used in tail gas cleanup units since it is desirable to slip as much CO_2 as possible while absorbing the maximum amount of H_2S to be recycled back to the Claus unit. Mixed amines are typically mixtures of MDEA and DEA or MEA which enhance CO_2 removal while retaining desirable characteristics of MDEA such as reduced corrosion problems and low heats of reaction (Polasekjerri and Bullin, 1994).

MEA is effective at removing almost all hydrogen sulfide and carbon dioxide, but requires a large quantity of heat to regenerate. MEA is used when the specification requires maximum hydrogen sulfide and carbon dioxide removal, particularly at low pressure. MEA reacts with carbonyl sulfide and carbon disulfide, forming non-regenerative degradation products. DEA is used when the specification allows for some carbon dioxide to be left in the treated gas and suit for gas streams with less stringent product specifications. DEA does not form non-regenerative degradation products with carbonyl sulfide, which makes it a suitable choice for treating refinery gases.

MDEA is a weak base that reacts much faster with hydrogen sulfide than with carbon dioxide, making it particularly selective under the proper design conditions. MDEA is used selectively on higher-pressure gas streams (20.6 Bar G. and above) for deep hydrogen sulfide removal with only moderate carbon dioxide removal. MDEA can also be used non-selectively for bulk removal of carbon dioxide from gas streams, but bulk removal requires the aid of absorption enhancing additives. MDEA is well suited for selective absorption on high-pressure gas streams (Wittenemann, 2008).

2.4 ACID GASES

Acid gas is component of natural gas that contains significant amounts of hydrogen sulfide (H_2S), carbon dioxide (CO_2), or similar contaminants. Small amounts of hydrogen sulfide occur in crude petroleum, but natural gas can contain up to 90%. Natural gas is usually considered sour if there are more than 5.7 milligrams of H_2S per cubic meter of natural gas, which is equivalent to approximately 4 ppm by volume (Gas Malaysia). Table 2.3 shown the typical composition of natural gas mixture from Qatar which contain quite large amount of sour gas.

H_2S is a colorless, flammable, extremely hazardous gas with a “rotten egg” smell. Some other names for H_2S are sewer gas, stink damp, swamp gas and manure gas. It occurred naturally in natural gas and produced by bacterial breakdown of organic materials and human and animal wastes. H_2S not only has an unpleasant odour, but also is highly poisonous, being almost as toxic as hydrogen cyanide and five to six times toxic as carbon monoxide. H_2S is slightly heavier than air; a mixture of H_2S and air is explosive. H_2S is soluble in water and acts as a weak acid. A solution of H_2S in water is initially clear but over time turns cloudy. This is due to the slow reaction of H_2S with the oxygen dissolved in water, yielding elemental sulfur which precipitates out. When burned it produces sulphur dioxide (SO_2), which is also obnoxious and corrosive. Its presence in synthesis gases may result in catalyst poisoning and product contamination (M. Reeid & C. Updegraff, 1950).

CO_2 is a chemical compound composed of two oxygen atoms covalently bonded and one single carbon atom that exist in gas phase at standard temperature and pressure. CO_2 is colorless and non-flammable. At low concentrations, the gas is odorless. At higher concentrations it has a sharp, acidic odor. CO_2 present in the natural gas need to be removed in other to increase the heating value of the gas, prevent corrosion of pipeline and gas process equipment and crystallization of CO_2 during cryogenic process (liquefaction process).

Table 2.3 Typical composition of natural gas mixture. A sample was taken from Qatar's North Field (Qatargas, 2002)

| Component | Mole Fraction |
|------------------|---------------|
| Nitrogen | 3.97 |
| H ₂ S | 0.96 |
| CO ₂ | 2.45 |
| Methane | 82.62 |
| Ethane | 4.84 |
| Propane | 1.78 |
| i-Butane | 0.39 |
| n-Butane | 0.67 |
| i-pentane | 0.29 |
| n-pentane | 0.27 |
| n-hexane | 0.34 |
| H ₂ O | 1.42 |
| Total | 100 |

2.5 ACID REMOVAL PROCESS

Varieties of processes and improvement have been developed over the years to treat certain types of gas with the aim of optimizing capital cost and operating cost, meet gas specifications and for environmental purpose. There are many type of treating the acid gas from natural gas. These processes are including chemical solvents, physical solvents, and adsorption processes hybrid solvent and physical separation (membrane). The main processes are based on absorption, and selectivity of the solvent with respect to acid gases is based on an affinity of the chemical or physical type.

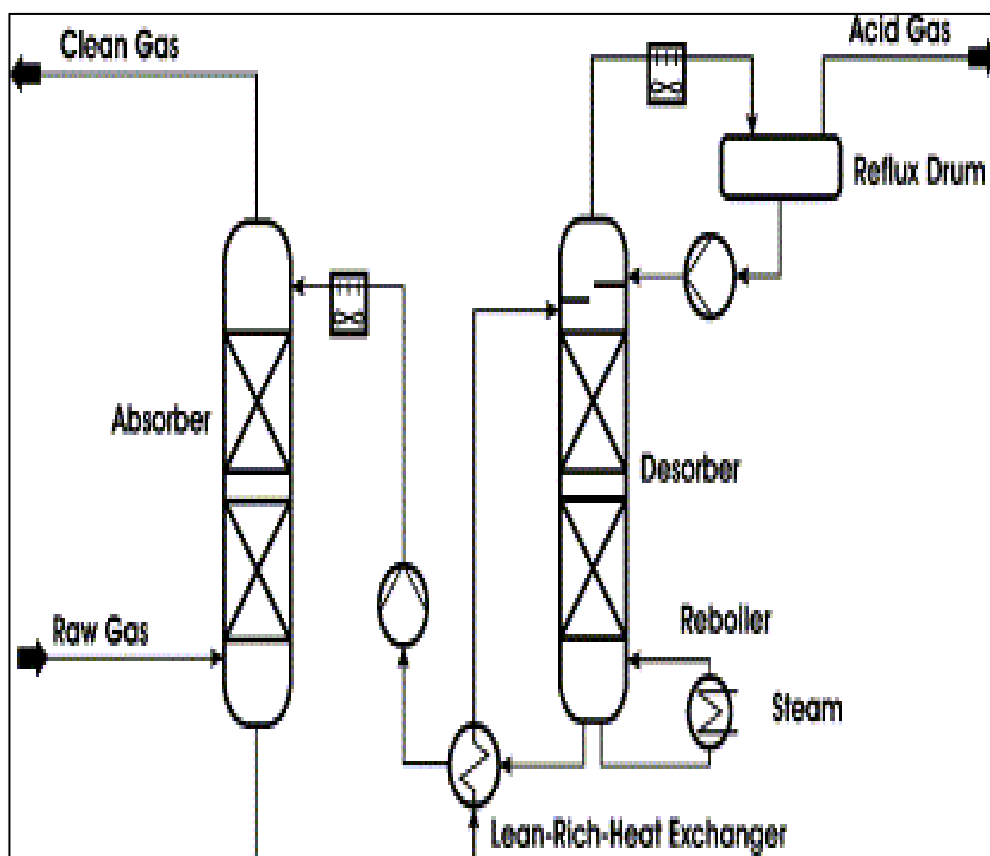


Figure 2.1 Schematic of simple acid gas removal unit
(Nordenkamp, 2003)

From figure 2.1, the sour gas is entered in the absorber where it contacts with amine solution flowing down the column. The acid gas components, H_2S and CO_2 are absorbed by the amine solution and sweet gas leaves the absorber for advance processing. The absorber allows counter-current flow of lean amine from the top and sour gas from the bottom. The rich amine is flow to the bottom while the sweet gas is collected at the top for further processing.

The throttling valve is used to expand the rich amine coming from the high pressure contactor; this is done by lowering gas pressure before entering the flash tank. The rich amine that contains the acid gases is sent to a stripper or regenerator. The rich amine is stripped at low pressure to remove the absorbed acid gases, dissolved hydrocarbon, and water.

Finally, a heat exchanger cools the lean solution before completing the loop back to the absorber and entering the absorber. The rich/lean exchanger is a heat conservation device where hot lean solvent preheats cooler rich solvent. The lean amine solvent from the re-boiler through heat exchanger is further cooling before entering the absorber again. The reflux and pump is installed to maintain the recycle lean solvent at the desired operating pressure of the absorber.

In solvent absorption, the two main cost factors are the solvent circulation rate, which affects both equipment size and operating costs, and the energy requirement for regenerating the solvent. The advantages of using amines technology are ability to reduce the concentration of H_2S and CO_2 to ppm levels and relatively insensitive to H_2S and CO_2 partial pressure.